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Lab-on-a-Chip Analysis of Explosives

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Introduction: Laboratory analysis of complex "real-world" samples typically requires a series of time-consuming and labor-intensive steps that include sample preparation, separation, and detection. The emerging technology of microfluidic analytical devices, or "Lab-on-a-Chip" (LOC), allows these functions to be integrated onto a single compact platform. Such devices, due to the design simplicity available through advanced microfabrication technologies, permit the integration of various functional elements such as sample preparation and handling, sample loading, separation, and detection, onto a single microchip platform. Typical analytical microsystems rely on electrokinetic fluid "pumping" of the sample through a network of channels patterned in a planar (glass or plastic) substrate, eliminating the need for external pumps or valves. Microchip capillary electrophoresis (CE) has been shown to provide high-speed analysis with improved separation efficiencies, therefore, are very attractive for addressing some of the security needs currently facing our troops. These needs include the sensitive and selective detection of explosives, whether in oceanic environments (e.g., mines), or as improvised explosive devices (IED). Despite the advantages afforded by these devices, the reduced microfluidic channel dimensions directly affect the sensitivity of most traditional detection technologies and require integrating additional sample preconcentration techniques onto the microchip platform. We discuss the successful application of LOC to the analysis of explosive mixtures. We examine the integration of on-chip solid phase extraction (SPE) techniques for dramatic enhancements in sensitivity.

Microchip Design: Figure 1(a) shows the microchip design for integrating solid phase extraction on a packed bed of beads, the subsequent elution of analytes using an organic eluent, injection, separation, and detection. The channels (20-µm deep by 60-µm wide) are etched in a glass substrate and bonded with a cover glass plate to close the microfluidic network. All fluid flow is controlled electro-osmotically by the application of desired voltages to the individual reservoirs. A typical SPE injection sequence consists of first directing the sample across the micro-SPE column to the sample waste reservoir. This is followed by elution

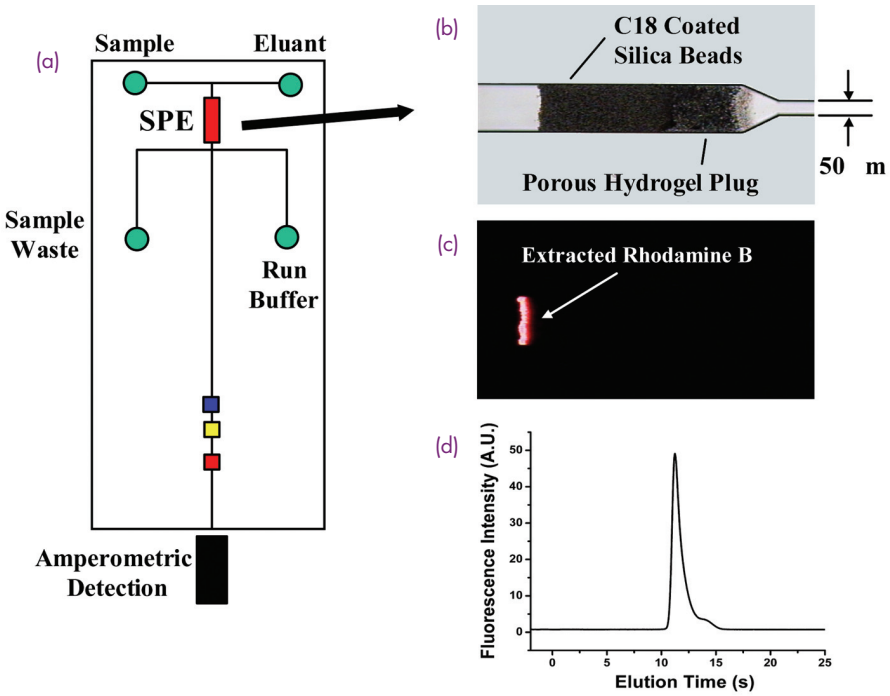

FIGURE 1
(a) SPE microchip design; (b) close-up of packed bed; (c) fluorescence microscope image of Rhodamine B loading onto packed bed; and (d) electropherogram for micro-SPE of 100 pM Rhodamine B.

of a concentrated band of analytes via subsequent application of voltage to the eluent reservoir. The eluted sample plug is introduced into the separation channel by application of another voltage sequence, leading to its separation into individual analyte bands using the appropriate run buffer.

Explosives Analysis on a Microchip: Because of their electrical neutrality, the electrophoretic separation of nitroaromatic explosives requires the introduction of a pseudo-stationary phase in the form of a surfactant added to the run buffer. Figure 2 shows a CE microchip separation of five different nitroaromatic explosives in the absence of any SPE. The electrochemical activity of nitro-functional groups permits amperometric detection of the separated bands as they elute from the end of the microchip. Despite the similarity in structure between these different aromatic explosives, the high resolving power of the LOC permits near-baseline resolution in just 100 s.

Solid Phase Extraction (SPE) on a Microchip: Although TNT (2,4,6-trinitrotoluene) and DNB (1,3-dinitrobenzene) detection limits have been achieved down to 60 ppb,[1] the demanding sensitivity requirements of explosive sensors in oceanic environments prompted us to investigate the incorporation of SPE techniques[2] directly on the microchip platform. Figure 1(b) is a close-up image of the micro-SPE bed. To contain the packing material, 5-μm C_{18} coated silica beads, within a microfluidic platform, a porous poly(methacrylate) polymer was synthetically crosslinked inside the channel by ultraviolet (UV) photoinitiation. Although the fluorescence image shown in Fig. 1(c) visually demonstrates the successful extraction of Rhodamine B (a model dye compound with similar hydrophobicity to aromatic explosives) onto a micro-SPE bed, the electropherogram shown in Fig. 1(d) for the on-chip SPE extraction and elution of a 100-pM sample dye indicates that the detection limits can be lowered into the femtomolar range. The quantitative nature of the extraction process is illustrated in Fig. 3(a). As expected, a linear increase in the fluorescence intensity of the eluted Rhodamine B was observed with increasing extraction time. The preconcentration factors range from 20 to 300 times, but it can be much larger, depending on the total extraction time. When coupled to the separation step, it is possible to concentrate and separate a series of neutral fluorescent dyes (Fig. 3(b)) in an experiment analogous to that needed for the detection of nitroaromatic explosives.

Summary: We have demonstrated successful direct coupling of micro-SPE enrichment with advanced separation techniques for model dye compounds. Efforts are underway to couple enrichment technologies with microseparation devices for the separation of nitroaromatic explosive mixtures, investigations which should ultimately lead to powerful detection schemes for explosives and other toxic analytes of concern to the DoD and analytical community alike.

[Sponsored by ONR and MIPT]

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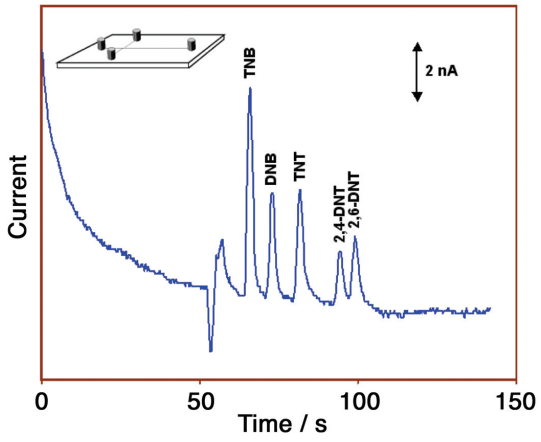
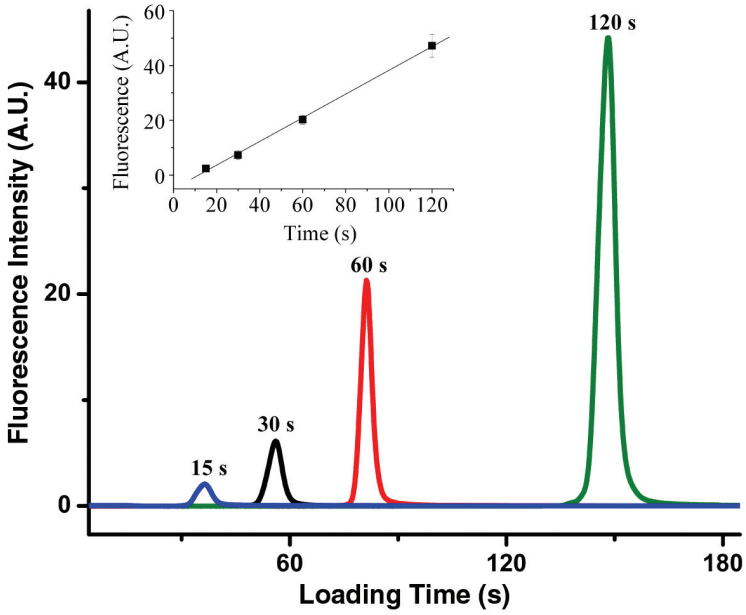
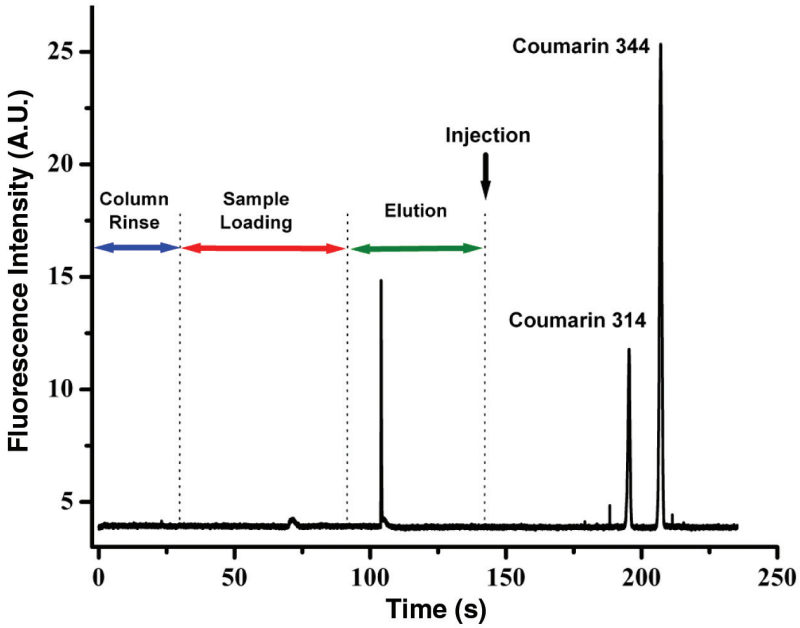


FIGURE 2
Microchip capillary electrophoretic separation and amperometric detection of five nitroaromatic explosives (2 ppm each). DNB = 1,3-dinitrobenzene; TNT = 2,4,6-trinitrotoluene; 2,4-DNT = 2,4-dinitrotoluene; 2,6-DNT = 2,6-dinitrotoluene.



(a)



(b)

FIGURE 3
(a) Microchip SPE of 250-nm Rhodamine B for sequentially increasing load times; (b) microchip separation of two neutral dyes following on-chip SPE.